TEMASEK
JUNIOR COLLEGE

CHEMISTRY (H2) **9647/03**

Paper 3 Free Response

Tuesday **16th September 2014** **2 hours**

Candidates answer on separate paper.

Additional materials: Answer paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group and Index number in the spaces provided on the cover page and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

This question paper consists of 15 printed pages.

Answer any **four** questions.

1 (a) The table below shows the melting points of aluminium fluoride, aluminium chloride and silicon tetrachloride.

Compound	Melting point/ °C
Aluminium fluoride	1290
Aluminium chloride	190
Silicon tetrachloride	-90

(i) Explain the difference in their melting points in terms of their structure and bonding.

- AlF_3 has a **<u>giant ionic structure</u>** with **<u>strong ionic bonds</u>** present between Al^{3+} and F^-. Large amount of energy is required to overcome the strong ionic bonds.
- $SiCl_4$ and aluminium chloride have **<u>simple molecular structure</u>**. **<u>Less energy</u>** is required to overcome the **<u>van der Waals' forces</u>** present between the molecules.
- $AlCl_3$ **<u>dimerises</u>** to form Al_2Cl_6. Since Al_2Cl_6 has a **<u>larger and more polarisable electron cloud, stronger and more extensive van der Waals' forces</u>** of attraction exist between the molecules.

(ii) With the aid of equations, explain the reactions that take place when silicon tetrachloride and aluminium chloride are mixed with excess water.

- $SiCl_4$ undergoes **<u>hydrolysis</u>** with water using the **<u>energetically accessible vacant 3d orbitals</u>** in Si.
- $SiCl_4(s) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl\ (g)$

  Or $SiCl_4(s) + 4H_2O(l) \rightarrow SiO_2.2H_2O(s) + 4HCl\ (g)$

  (Note: do not accept $Si(OH)_4$ as product)
- $AlCl_3$ undergoes **<u>hydration and hydrolysis</u>**. The **<u>high charge density of aluminium ion polarises water molecules</u>**, weakening the O-H bond and causing it to break.
- $AlCl_3(s) + aq \rightarrow Al^{3+}(aq) + 3Cl^-(aq)$

  $[Al(H_2O)_6]^{3+} \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H^+$

[7]

(b) Silver chloride is sparingly soluble in water.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

(i) Briefly describe any difference in the solubility of silver chloride in water and in aqueous aluminium chloride.

- AgCl will be **<u>less soluble in aqueous $AlCl_3$</u>** due to **<u>common ion effect or higher concentration of chloride ions</u>** in the solution. By Le Chatelier's Principle, **<u>position of equilibrium shifts to the left</u>**.

(ii) Given that the solubility product of silver chloride is 1 x 10^{-10} $mol^2\ dm^{-6}$, calculate the maximum [Ag^+(aq)] before a precipitate starts to form in 0.0500 mol dm^{-3} of aqueous aluminium chloride.

- [Cl^-] = 0.150 mol dm^{-3}

  Ionic product = K_{sp}
- [Ag^+][Cl^-] = 1 x 10^{-10}

  [Ag^+] = 1 x 10^{-10} / 0.150 = 6.67 x 10^{-10} mol dm^{-3}

Silver ions form complexes with ammonia and with amines.

$$Ag^+(aq) + 2RNH_2(aq) \rightleftharpoons [Ag(RNH_2)_2]^+(aq)$$

(iii) Write a K_C expression for this reaction and state its units.

- $K_C = [Ag(RNH_2)_2{}^+]/[Ag^+][RNH_2]^2$ $mol^{-2}\ dm^6$

(iv) K_C has a numerical value of 1.7 x 10^7 when R = H. Using your expression for K_C, calculate the [NH_3(aq)] needed to change the [Ag^+(aq)] in a 0.010 mol dm^{-3} solution of silver nitrate to the value that you calculated in **(b)(ii)**.

Since the final [Ag^+(aq)] is very low, we can assume that most of the Ag^+(aq) has gone to the complex and the change in [NH_3] is minimal ie

[Ag^+(aq)] = 6.67 x 10^{-10} mol dm^{-3}

[$Ag(NH_3)_2{}^+$] = 0.01 mol dm^{-3}

- [NH_3] = $\sqrt{\{[Ag(NH_3)_2{}^+]/(K_c[Ag^+])\}}$
  = $\sqrt{\{0.01/(1.7 \times 10^7 \times 6.67 \times 10^{-10})\}}$
- = 0.939 mol dm^{-3}

Other acceptable working:

	$Ag^+(aq)$ +	$2NH_3(aq)$ $\rightleftharpoons$	$[Ag(NH_3)_2]^+(aq)$
Initial conc/mol dm^{-3}	0.010	x	0
Change/mol dm^{-3}	-0.00999	-2(0.00999)	+0.00999
Equilibrium/mol dm^{-3}	6.67x10^{-10}	x – 0.0199 = x – 0.020	0.00999 = 0.01

[NH_3] = $\sqrt{\{[Ag(NH_3)_2{}^+]/(K_c[Ag^+])\}}$

(x - 0.020) = $\sqrt{\{0.01/(1.7 \times 10^7 \times 6.67 \times 10^{-10})\}}$

x = 0.939 + 0.020 = 0.959 mol dm^{-3}

(v) Explain whether you would expect the K_C for the reaction where R = C_2H_5 to be greater or less than that for the reaction where R = H. [8]

- When R = C_2H_5, **<u>K_C is likely to be greater</u>**.
- The **<u>electron releasing ethyl group</u>** will cause the **<u>lone pair on N to be more available</u>** for dative bonding to Ag^+ to form the complex.

(c) Compound **A** is a chloroalkane with the molecular formula C_4H_9Cl. Compound **A** rotates plane of polarised light. When compound **A** is reacted with aqueous sodium hydroxide, an optically inactive product is obtained.

(i) Deduce the identity of compound **A**.

- Since compound **A** rotates the plane of polarised light, it has a **chiral centre** and has no plane of symmetry in the molecule.
- Compound **A** is 2-chlorobutane.

(ii) Deduce the type of reaction that has taken place when compound **A** is reacted with aqueous sodium hydroxide.

- A **racemic mixture** is obtained when compound **A** is reacted with aqueous sodium hydroxide, indicating that there's an equal probability of nucleophile attacking from top or bottom of the carbocation. Hence compound **A** has undergone **S_N1 reaction**.

(iii) With the aid of Data Booklet, explain how the rate of this reaction changes, if any, when the chloroalkane is replaced by an iodoalkane. [5]

- Bond energies: C – I = 240 kJ mol^{-1}, C – Cl = 340 kJ mol^{-1}
- The **C-I bond is weaker**, so the rate determining step of nucleophilic substitution reaction i.e. breaking of C – I bond, will be faster for the iodoalkane. The rate of reaction will be **faster.**

[Accept if student quote atomic radius of I (0.133nm) and Cl (0.099nm) and explains that orbital overlap will be less effective for C – I and so weaker.]

[Total: 20]

2 This question is about magnesium and its applications.

(a) Magnesium does not occur naturally in its elemental form. One method to produce elemental magnesium involves the thermal reduction of magnesium oxide.

(i) Predict, with reasoning, whether the melting point of magnesium oxide is higher or lower than that of the Group II oxides further down the group.

- **MgO has a higher melting point as compared to the Group II oxides down the group.**
- **The strength of ionic bonds is indicated by the lattice energy of the Group II oxides. Down the group, the ionic radii of the Group II cations increase while the charge remains constant. As lattice energy $\propto \left|\frac{q^+q^-}{r^+ + r^-}\right|$, lattice energy for the Group II oxides down the group is less exothermic, hence less energy is required to break the ionic bonds in the lattice.**

Magnesium oxide can be formed the decomposition of magnesium carbonate on heating.

(ii) Write an equation for the decomposition of magnesium carbonate.

$MgCO_3 \rightarrow MgO + CO_2$

(iii) State and suggest an explanation for the trend observed in the thermal stability of the Group II carbonates.

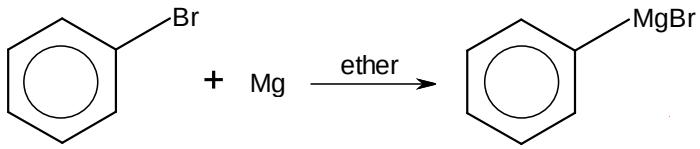
- **Down the group, thermal stability of Group II carbonates increases.**
- **Down the group, charge of the cation remains constant but ionic radius increases. Hence <u>charge density of the cation decreases</u>.**

  <u>Polarising power of cation decreases</u>, resulting in <u>less distortion</u> of the <u>electron cloud</u> of CO_3^- ion, weakening the C-O covalent bond less. Hence, more heat energy is required to decompose the carbonates down the group.

[5]

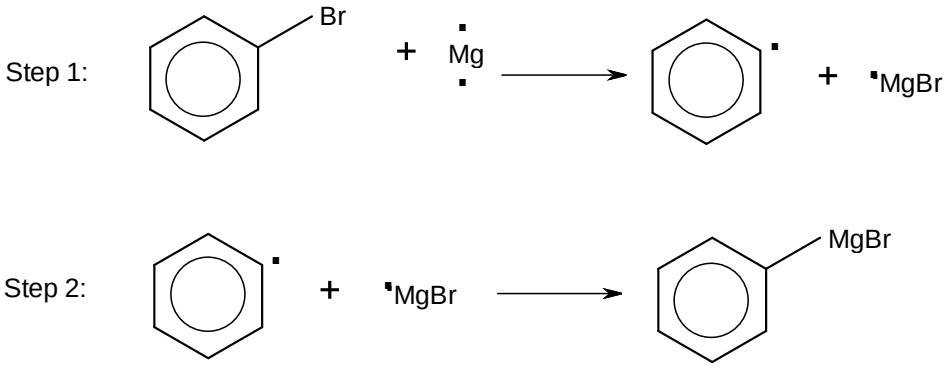
Grignard reagents are useful organometallic reagents in organic synthesis, as it provides a convenient source of alkyl nucleophile (R^-) that can attack an electron deficient carbon in organic functional groups such as carbonyls.

One example of a Grignard reagent is phenylmagnesium bromide, which can be prepared by the reaction of magnesium metal (in excess) with bromobenzene using dry ether as the solvent:



(b) The formation of Grignard reagents from aromatic halides takes place on the surface of the magnesium metal. The mechanism of this reaction is thought to involve two steps:

- There is a transfer of a single electron from the magnesium surface to the halogen, followed by homolytic fission of the C_6H_5–Br bond to give $C_6H_5^{\bullet}$, $Mg^{\bullet+}$ and Br^-. Br^- immediately combines with the electron deficient $Mg^{\bullet+}$ to give a surface-bound radical, $MgBr^{\bullet}$.
- The two radicals then react together to give C_6H_5MgBr.



(i) Explain what is meant by the term *free radical*.

- **Free radical refers to an atom or group of atoms with <u>an unpaired electron</u> and is <u>highly reactive</u>.**

(ii) Suggest which step in the mechanism above is the rate-determining step. Explain your reasoning.

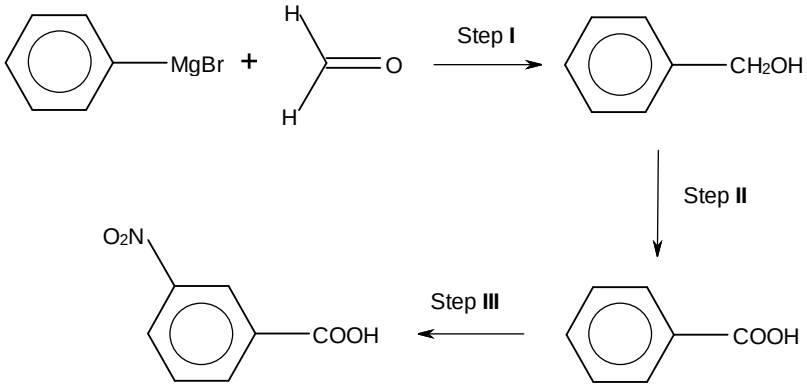
- **Step 1 is the rate-determining step.**
- **Step 1 involves single electron transfer from Mg and homolytic fission of the C–Br bond in C_6H_5Br, which requires energy. Step 2, on the other hand, is a reaction between two reactive radicals.**
  (From Data Booklet, 1st IE of Mg: 736 kJ mol^{-1} and C–Br bond: 280 kJ mol^{-1})

  [Alternative answer for 2nd mark:
  Step 1 involves bond breaking while step 2 involves bond forming
  (Award 2nd mark so long as student recognises that step 1 requires energy due to single electron transfer or homolytic fission)

[3]

(c) 3-nitrobenzoic acid is an important precursor in pharmaceutical and organic synthesis.

It can be synthesised from phenylmagnesium bromide via the following reaction scheme:



(i) Suggest reagents and conditions for Steps **II** and **III**.

Step II: Reagents and conditions: Acidified $KMnO_4$, heat or reflux

OR acidified $K_2Cr_2O_7$, heat or reflux.

Step III: Reagents and conditions: concentrated HNO_3 and concentrated H_2SO_4, reflux at temp $\leq$ 60°C

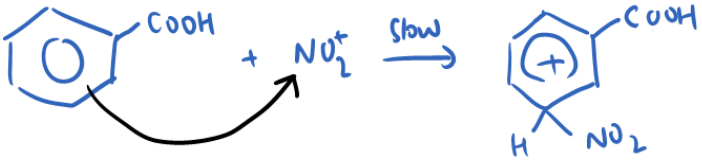
(ii) Describe the mechanism for the reaction in Step **III**.

Mechanism:

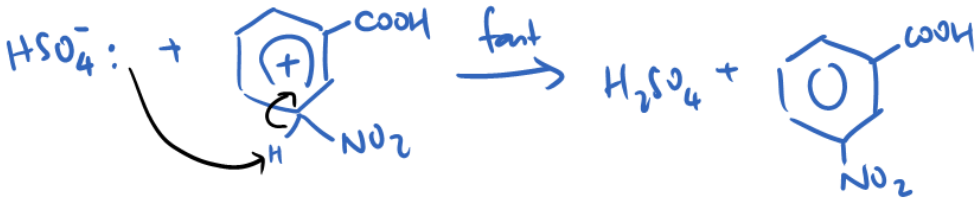
- **Step 1**

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$$

- **Step 2**

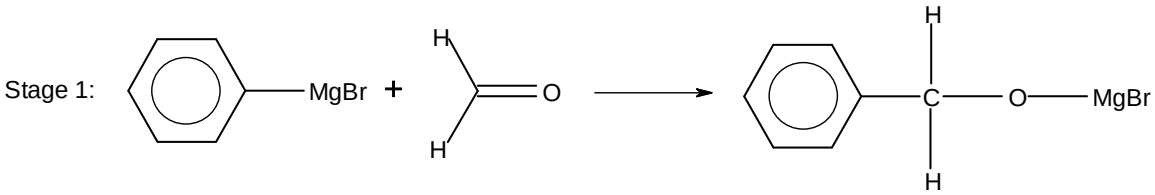


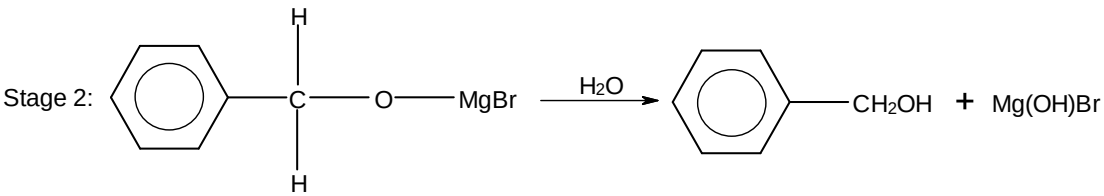
- **Step 3**



[Note: 1 m for each step. 0 m if did not show lone pairs, movement of electrons, and/or relevant charges where applicable.]

(iii) Step **I** is an example of nucleophilic addition, which proceeds via two stages.





The reaction kinetics of the reaction was investigated, and the following data was obtained.

Experiment	Initial [C_6H_5MgBr] / mol dm^{-3}	Initial [HCHO] / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} min^{-1}
1	0.30	0.40	0.0240
2	0.10	0.40	0.0080
3	0.20	0.60	0.0240

Use these data to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction.

From experiments 1 and 2,

When [HCHO] is constant and [C_6H_5MgBr] is decreased by 3 times, initial rate also decreases by 3 times.

- **Therefore, the order of reaction with respect to C_6H_5MgBr is 1.**

From experiments 2 and 3,

$0.0080 = k\,(0.10)(0.40)^x$ -------(1)

$0.0240 = k\,(0.20)(0.60)^x$ --------(2) On solving, x = 1

- **Therefore, the order of reaction with respect to HCHO is 1.**
- **Rate = k[C_6H_5MgBr][HCHO]**

(iv) The variation of the rate constant, *k*, for Step **I** with temperature, *T*, is given by the following equation:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where E_a denotes the activation energy in J mol^{-1}, R is the gas constant, and T is the temperature in Kelvin.

Given that the rate constant and activation energy of Step **I** is 9.16×10^{-3} mol^{-1} dm^3 s^{-1} and +102 kJ mol^{-1} at 25 ^oC respectively, show, using calculations, the effect of temperature change on the rate of the reaction when the temperature is raised by 5 ^oC.

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

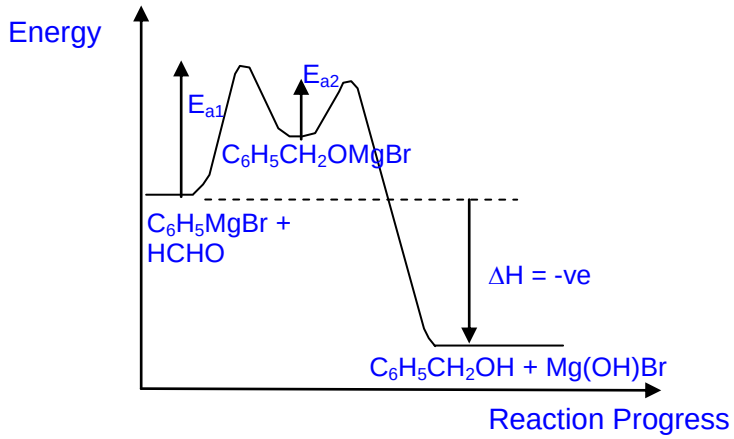
$$\ln\frac{k_2}{9.16 \times 10^{-3}} = -\frac{102000}{8.314}\left(\frac{1}{303} - \frac{1}{298}\right)$$

$$k_2 = 1.97 \times (9.16 \times 10^{-3})$$

- $k_2 = 1.81 \times 10^{-2}\ mol^{-1}dm^3\ s^{-1}$

A rise in temperature of 5 ^oC results in <u>a larger rate constant ($k_2 > k_1$)</u>. Since the concentrations of the reactants are kept constant, a larger rate constant would indicate a • <u>faster</u> reaction.

(v) Draw a labelled energy profile diagram for Step **I**, given that the reaction is exothermic.



Marking points: •*Correct E_{a1}, E_{a2} ($E_{a1} > E_{a2}$)* •*Correct ΔH*
Note: -1m if labelling of axes is wrong/ if didn't label reactants and products

[12]

[Total: 20]

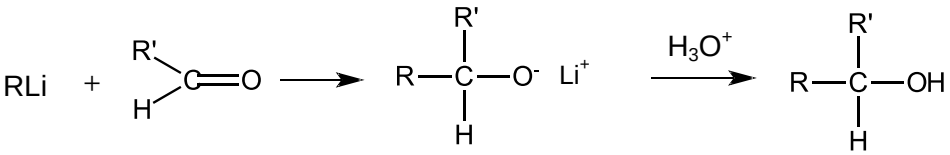
3 Sodium propanoate, represented by the food labeling E281 in Europe, is used primarily as a mould inhibitor in bakery products.

(a) Sodium propanoate can be prepared in a synthesis involving an organometallic compound known as organolithium compound.

Organolithium compounds, RLi, are usually prepared by the reaction of an alkyl halide and lithium metal in an ether solvent such as diethyl ether Et_2O.

$$RX + 2Li \xrightarrow{Et_2O} RLi + LiX$$

The following reaction shows how an organolithium reagent can be added to a carbonyl compound to prepare an alcohol.



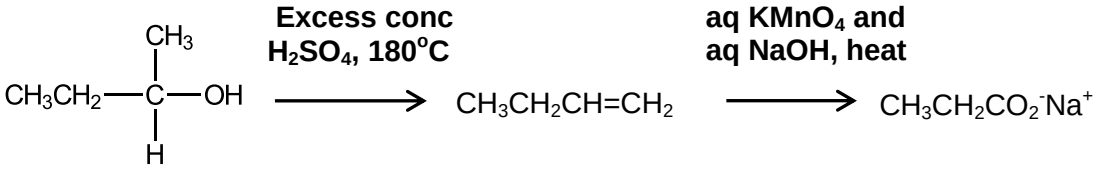
(i) Suggest the organolithium reagent required to convert ethanal into butan-2-ol.

- **CH_3CH_2Li**

(ii) Having obtained butan-2-ol, propose how you would convert it to sodium propanoate.

- **Heat butan-2-ol with aqueous iodine and aqueous NaOH**

OR



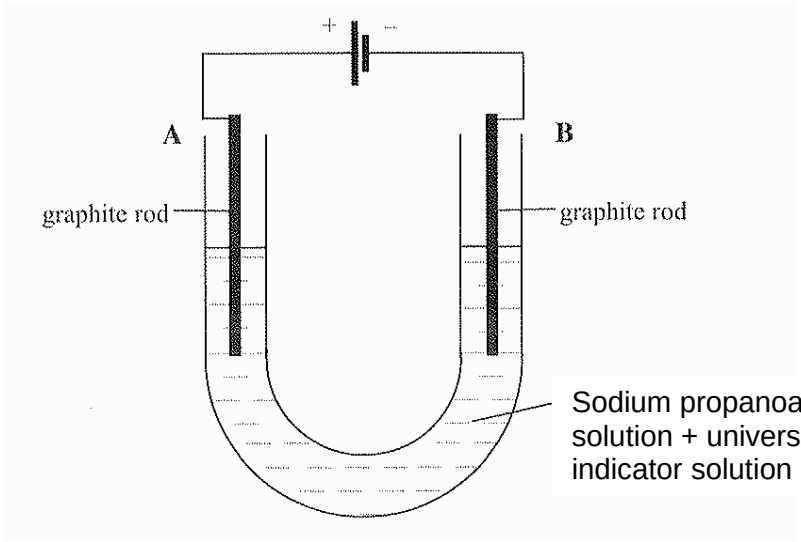
[alternatively, can use acidic $KMnO_4$, heat, followed by excess aq NaOH in step 2 of second proposal]

[2]

(b) Sodium propanoate can be used to prepare butane by an electrochemical reaction, which is known as the Kolbe electrolysis reaction. Butane is formed at the anode by the following reaction:

$$2C_2H_5\text{-}CO_2^- \rightarrow C_4H_{10} + 2CO_2 + 2e^-$$

A student investigated the electrolysis of aqueous solution of sodium propanoate, using graphite electrodes in the apparatus shown below.



(i) State and explain any colour change expected at electrode **B**, and construct an equation for the **overall** reaction.

At the cathode: $\mathbf{2H_2O + 2e^- \rightarrow H_2 + 2OH^-}$

- **The product OH^- turns the universal indicator purple (or blue).**

- **Overall reaction:** $\mathbf{2\ C_2H_5\text{–}CO_2^- + 2H_2O \rightarrow\ C_4H_{10} + 2CO_2 + H_2 + 2OH^-}$

(ii) Calculate the time, in minutes, taken by the student to pass current of 5.0 A through a solution of sodium propanoate to produce 1.50 g of butane.

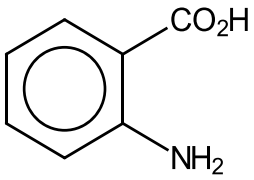
No of moles of butane = 1.5/58 = 0.0259 mol

- **No of moles of electrons = 0.0259 x 2 = 0.0518 mol**

- **time = Q/I = $\frac{0.0518 \times 96500}{5 \times 60}$ = 16.7 min**

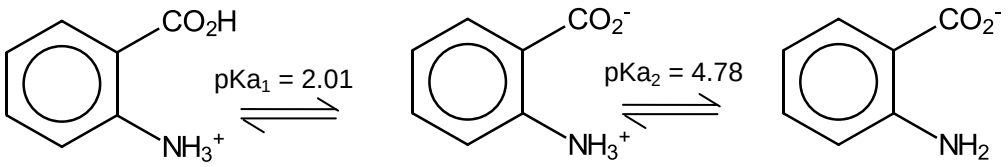
[4]

Anthranilic acid, a derivative of benzoic acid, is used as an intermediate for production of dyes, pigments and saccharin.

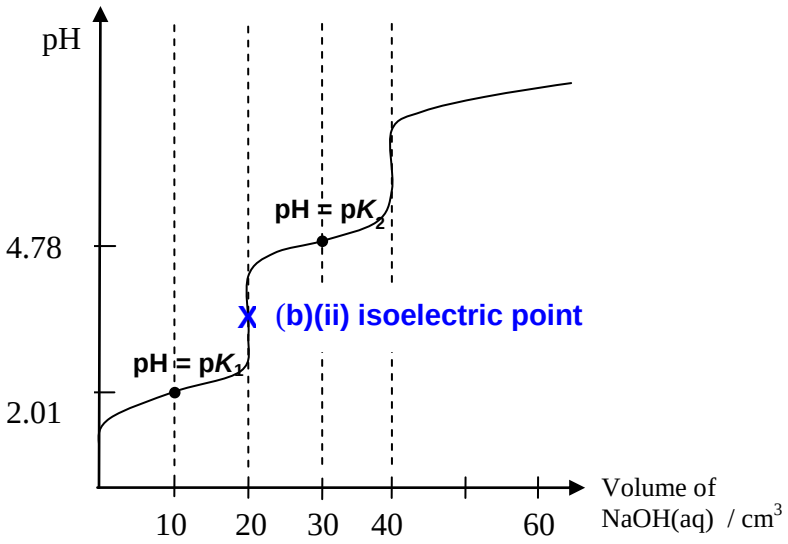


anthranilic acid

(c) (i) The two pK_a values associated with anthranilic acid are 2.01 and 4.78.



Sketch the titration curve when 20 cm^3 of protonated form of anthranilic acid is being titrated with 60 cm^3 of NaOH(aq) of the same concentration. Your sketch should show clearly where the two pK_a values occur.



[1] Correct shape of curve and labelling of axes
[1] 2 neutralisation points at volumes 20 cm^3 and 40 cm^3
[1] 2 max buffer capacity at pH values corresponding to the two given pK_a values 2.01 and 4.78 at volumes 10 cm^3 and 30 cm^3 respectively.

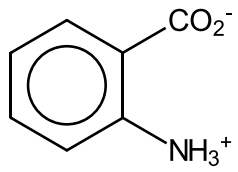
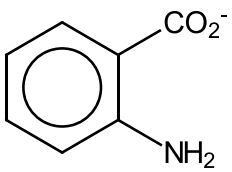
(ii) Indicate clearly the isoelectric point of anthranilic acid on your sketch with an "**X**".

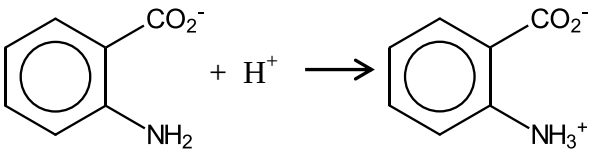
Isoelectric point indicated with X at mid-point of 1st equivalence point at volume of 20 cm^3 [1]

Anthranilic acid can function as a buffer in aqueous solution.

(iii) Suggest the structures of the species present in a solution of anthranilic acid at pH 4.78.

Hence write an equation to illustrate how this solution can act as a buffer when a small amount of $H^+(aq)$ is added.

-  and 

- 

[For buffer equation, only protonation of $-NH_2$ group accepted, not $-CO_2^-$]

(iv) A solution of anthranilic acid at pH 4.78 contains 0.005 mol of each of the 2 species in **(c)(iii)**.

Calculate the final pH if 0.001 mol HC*l* was added to the solution.

You may represent the acid as HA and the conjugate base as A^- in your working.

	A^-	**+ H^+**	**→**	**HA**
Before adding H^+/ mol	**0.005**			**0.005**
H^+ added / mol		**+0.001**		
After adding H^+ / mol	**0.005 – 0.001 = 0.004**			**0.005 + 0.001 = 0.006**

(1m for working)

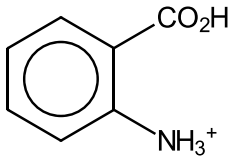
pH = pKa_2 + lg $[A^-]/[HA]$

= 4.78 + lg (0.004/0.006)

- = **<u>4.60</u>**

[8]

(d) The structure below shows the protonated form of anthranilic acid:



When an aromatic compound, **B**, with molecular formula $C_{10}H_{11}NO$ is refluxed with acidified potassium manganate(VII), the protonated form of anthranilic acid and another acidic organic product, **C**, with molecular formula $C_3H_4O_3$ are formed. No other organic compound is formed in the oxidation. Both compounds **B** and **C** react with 2,4-dinitrophenylhydrazine. Compound **B** reacts readily with 3 moles of Br_2(aq) to form compound **D**, $C_{10}H_{10}NO_2Br_3$. Compound **B** also reacts with hot alkaline aqueous iodine to form compound **E**, $C_9H_8NO_2Na$.

Deduce the structures of **B, C, D** and **E.** Explain your deductions.

½ **C is acidic, suggesting that it <u>has $-CO_2H$</u> or is <u>carboxylic acid.</u>**

½ **Since C also reacts with 2,4-dinitrophenylhydrazine and is a product of strong oxidation, it is <u>a ketone not aldehyde.</u> Based on formula, C is:**

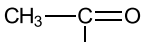
- **CH_3COCO_2H**

½ **B reacts with 2,4-dinitrophenylhydrazine, so it could be an <u>aldehyde or ketone</u>**

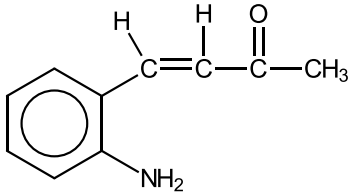
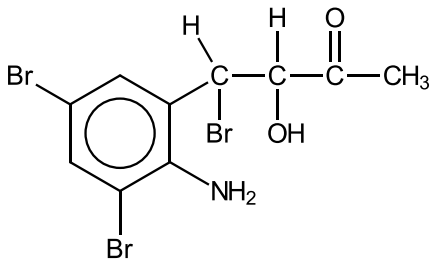
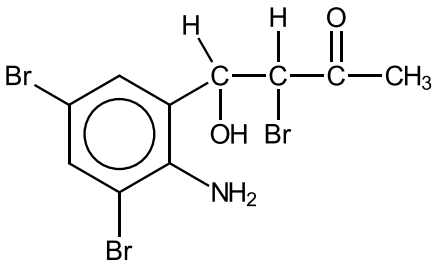
½ **Since B is oxidised by manganate(VII) to give protonated anthranilic acid and C, B could be <u>an alkene</u>.**

½ **With aq Br_2, one Br atom and one OH atom are added at the <u>carbon-carbon double bond</u> of B (or confirm B has <u>alkene</u> group).**

½ **Since D has 3 Br atoms, the remaining 2 Br atoms are at the benzene ring, implying that B is a <u>phenylamine/ has</u> <u>activating group like NH_2 bonded to benzene</u> and the 2- and 4- positions with respect to NH_2 group are unsubstituted.**

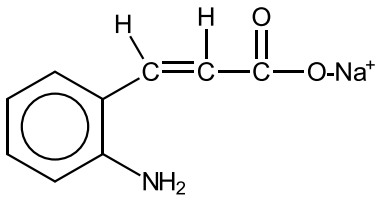
½ **B is oxidised by alkaline aq iodine, suggesting that it <u>has</u>**  **<u>group</u> and it forms a salt of carboxylic acid E.**

From the oxidised products, protonated anthranilic acid and C, we get B:

- **B**: 
- **D**:  or 

½

- **E**:



[6 + 2 bonus]

[Total: 20]

4 **(a)** Explain what is meant by the *tertiary structure* of a globular protein.

● Tertiary structure refers to the way a protein molecule <u>folds and bend</u> itself into a precise, <u>compact, globular three – dimensional shape</u>. It is <u>stabilized by the interactions between the R groups</u> of the amino acid.

[1]

(b) There are four types of R group interactions which hold the tertiary structure in its necessary shape. State **three** R group interactions and give an example of each.

Any three of the following:

- **hydrogen bonds between polar groups eg -O-H and -$CONH_2$ (or any other pair capable of hydrogen bonding except –CO_2H and –NH_2 groups)**
- **ionic bonds between oppositely charged groups eg –CO_2^- and -$^+NH_3$**
- **van der Waals' forces between non-polar R groups eg alkyl groups**
- **disulphide linkages between –SH groups**

[3]

(c) Describe how the R groups of the amino acid residues are arranged in a globular protein.

- **<u>Polar groups</u> such as <u>–CH_2OH, –CH_2COOH, –CH_2SH and –$(CH_2)_4NH_2$</u> will be located <u>on the surface</u> of the globular protein. The n<u>on-polar groups</u> such as <u>–CH_3</u> groups will be located <u>inside the protein</u> away from the aqueous surroundings**.

[1]

(d) Myoglobin (abbreviated Mb) is a single-chain globular protein of 154 amino acids, containing one heme group in the center around which the remaining protein folds. Myoglobin is an oxygen-carrier protein that occurs in muscle fibres. It has a higher affinity for O_2 than does haemoglobin, but only binds one O_2 molecule per Mb molecule, according to the following equation.

$$Mb(aq) + O_2(aq) \rightleftharpoons MbO_2(aq)$$

(i) Write an expression for K_c for this reaction, stating its units.

- **K_c =** $\dfrac{[MbO_2]}{[Mb][O_2]}$ • **Units: $mol^{-1}\,dm^3$**

(ii) Experiments have shown that when the $[O_2]$ = 8.80 x 10^{-6} mol dm^{-3}, the concentrations of MbO_2 and Mb are in the ratio 3:2

Use this information to calculate a value of K_c.

- **$K_c = \frac{[MbO_2]}{[Mb][O_2]} = \frac{3}{2(8.80 \times 10^{-6})} = 1.70 \times 10^5$ mol^{-1} dm^3**

Carbon monoxide binds with myoglobin more strongly than does oxygen. It is thought that the magnitude of K_c for carbon monoxide is about 100 times that of the value for oxygen. If the percentage of myoglobin that is combined with carbon monoxide reaches 20 %, the result is usually fatal to humans.

$$Mb(aq) + CO(aq) \rightleftharpoons MbCO(aq)$$

(iii) Calculate the fatal concentration of uncombined carbon monoxide in the body fluids.

Let y mol dm^{-3} be the initial concentration of Mb(aq)

	Mb(aq) + CO(aq) $\rightleftharpoons$	**MbCO(aq)**
Initial conc	**y**	
Equilibrium conc	**0.8y**	**0.2y**

- **[CO] = $\frac{0.2y}{0.8y \times 1.70 \times 10^5 \times 100}$ mol dm^{-3}**
- **= 1.47 x 10^{-8} mol dm^{-3}**

(iv) The fatal concentration to humans of carbon monoxide in air is quoted as 0.1%, by volume at rtp.

Comment on this figure compared with the value of fatal concentration in the body fluids calculated in **(d) (iii)**.

Fatal concentration of CO is 0.1%, by volume.

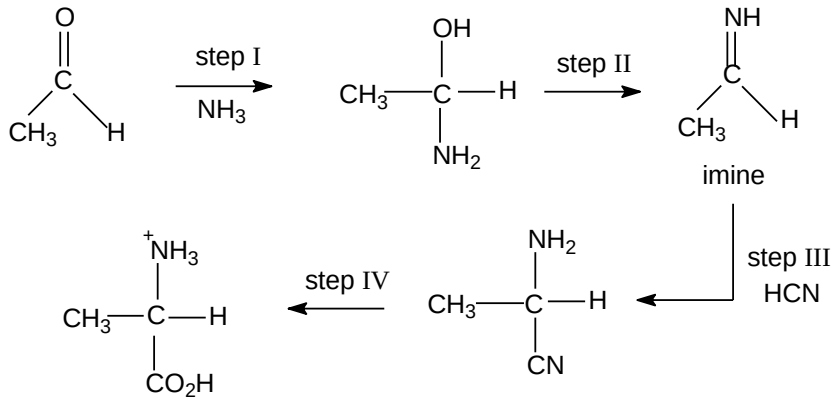
- **This is equivalent to 0.1 cm^3 of CO in 100 cm^3 of air.**

$\Rightarrow \frac{0.1 \times 10}{24{,}000}$ = 4.17 x 10^{-5} mol of CO per dm^3 of air

- **Hence the fatal concentration of CO is much lower in the body fluids compared to in the air.**

[7]

(e) The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker. Alanine, $CH_3CH(NH_2)CO_2H$ can be prepared from ethanal as a starting material as shown in the four steps reaction scheme below:



(i) Name the types of reactions in step I and step II.

- **Step I: Nucleophilic addition**
- **Step II: Elimination**

(ii) Suggest suitable reagents and conditions for step IV.

- **dil H_2SO_4 or dil HC*l*, heat or reflux**

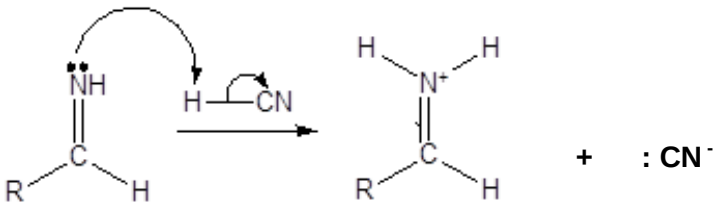
(iii) In step III, the reaction proceeds via 2 parts:

① Acid-base reaction between N in imine and HCN
② Followed by a nucleophilic attack on C by CN^-

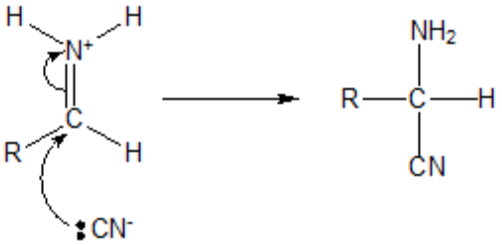
Propose a mechanism for step III, showing clearly the charges, lone pair of electrons and the movement of electrons using curly arrows.

●●

Step 1:



Step 2:

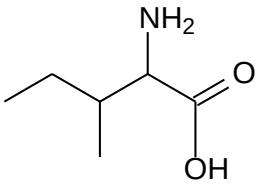


where R = CH_3

(iv) Suggest, with a reason, if there is any difference in the optical activity of a sample of amino acid synthesised by Strecker's method and that of a naturally occurring amino acid.

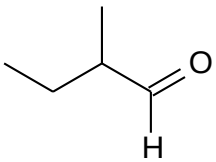
●● Strecker's synthesis produces a racemic mixture and hence, do not display optical activity while naturally occurring amino acid is present as one of the enantiomers (usually L enantiomer) and will rotate plane polarised light.

(v) Using Strecker's synthesis, identify the structural formula of the starting material, compound **Z** which can be used to prepare isoleucine.



isoleucine

●



Compound Z

[8]

[Total: 20]

5 This question is about the applications of manganese compounds.

(a) Modern phosphating is a process performed on iron parts for corrosion resistance and lubrication by forming a layer of insoluble, crystalline phosphate on the surface. Phosphates are generally insoluble except for Group I and ammonium phosphates.

For instance, manganese(II) phosphate coating is commonly used. Manganese(II) phosphate is first dissolved in phosphoric acid to form a saturated solution. The iron part is then immersed into the solution and reacts with the acid. This eventually results in the precipitation of manganese(II) phosphate on the surface of the iron part.

(i) Given that the numerical value of K_{sp} of manganese(II) phosphate, $Mn_3(PO_4)_2$, is 10^{-25}, determine the solubility of manganese(II) phosphate in phosphoric acid.

You may assume that the concentration of phosphate ions formed from full dissociation of phosphoric acid is negligible.

Let the solubility of $Mn_3(PO_4)_2$ be *x*.

$K_{sp} = [Mn^{2+}]^3[PO_4^{3-}]^2$
- $10^{-25} = (3x)^3(2x)^2$
- $x = 3.92 \times 10^{-6}$ mol dm^{-3}

(ii) Phosphoric acid is known to have the following pK_a values: 2.15, 7.20, and 12.35.

Write equations for the three stages of dissociation of phosphoric acid, and hence explain how the manganese(II) phosphate coating is formed on an iron part immersed in a saturated solution of manganese(II) phosphate in phosphoric acid.

- $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ ----------(1)
  $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ ----------(2)
  $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ ----------(3)

- When the iron part is immersed into the solution, the H^+ is consumed as it reacts with iron to form hydrogen gas and Fe^{2+} ions and $[H^+]$ decreases.
- By Le Chatelier's Principle, this causes the position of equilibrium of all three equilibria above to shift to the right. *(note: accept if just mention equilibrium 3)*
- This causes more PO_4^{3-} to be formed, therefore the ionic product of $Mn_3(PO_4)_2$ exceeds its K_{sp} and precipitation occurs on the surface of the iron part.

(iii) State and explain whether the coating is likely to be pure manganese(II) phosphate.

- It is unlikely to be pure, as iron(II) ions formed in the reaction with acid can possibly precipitate as iron(II) phosphate.

(iv) The hydrogen gas evolved during the process often adheres to the surface of the iron part as tiny bubbles, forming a layer that prevents acid from reaching the metal surface.

Nitrite ions, NO_2^-, are often pre-added to the solution to react with any hydrogen gas evolved to form ammonium ions and water. Construct a balanced equation for this reaction, showing your working.

- $NO_2^- + 8H^+ + 6e \rightarrow NH_4^+ + 2H_2O$
  $H_2 \rightarrow 2H^+ + 2e$ (x3)
- $NO_2^- + 3H_2 + 2H^+ \rightarrow NH_4^+ + 2H_2O$

Note: working must be shown. Either show the "x3" at the half-equation, or multiply it directly into the half-equation.

[9]

(b) Manganese(II) chloride is used in the production of dry cell batteries. When dissolved in water, manganese(II) ions are pale pink in colour.

(i) Explain why aqueous manganese(II) ions are coloured.

●Mn^{2+} has partially-filled d-orbitals. When the ligands approach the central metal ion, splitting of the d-orbitals occurs.

●The energy gap, ΔE, between the non-degenerate orbitals corresponds to the wavelength of light in the visible region of the electromagnetic spectrum.

●When an electron from a lower energy d orbital is promoted to a higher energy d orbital (d-d electron transition), radiation corresponding to ΔE is absorbed. The complementary colour will be seen as the colour of the complex.

(ii) A common test of the presence of manganese(II) ions is to add aqueous sodium hydroxide until in excess. A white precipitate of manganese(II) hydroxide will be formed, which will turn brown after some time in air.

In an experiment, this brown precipitate was filtered and analysed. It was found to contain 62.5 % of manganese, 36.4 % of oxygen and 1.1 % of hydrogen by mass. Determine the empirical formula of the precipitate. Hence, write a balanced equation for the formation of this brown precipitate from manganese(II) hydroxide.

Taking a basis of 100 g,

	Mn	O	H
Mass / g	62.5	36.4	1.1
Relative atomic mass	54.9	16	1
Number of moles	1.14	2.28	1.1
Simplest ratio	1	2	1

● Empirical formula is MnO_2H.

Note: Brown precipitate is actually MnO(OH). Equations can be written using deduced empirical formula.

$Mn(OH)_2 + OH^- \rightarrow MnO(OH) + H_2O + e$
$O_2 + 2H_2O + 4e \rightarrow 4OH^-$
● $4Mn(OH)_2 + O_2 \rightarrow 4MnO(OH) + 2H_2O$

[5]

(c) Alkaline batteries have a longer shelf life than conventional dry cells. The name is due to its alkaline electrolyte of potassium hydroxide, and alkaline batteries are dependent upon the reaction between manganese dioxide and zinc.

The ion-electron half equations are as follows:

$ZnO(s) + H_2O(l) + 2e \rightleftharpoons Zn(s) + 2OH^-(aq)$ $\quad E^{\ominus} = -1.28$ V

$2MnO_2(s) + H_2O(l) + 2e \rightleftharpoons Mn_2O_3(s) + 2OH^-(aq)$ $\quad E^{\ominus} = +0.15$ V

(i) Calculate the maximum amount of electrical energy that could be obtained from an alkaline battery.

$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{oxid}$

$= +0.15 - (-1.28) =$ ●+1.43 V

.Maximum amount of electrical energy = $n F E^{\ominus}_{cell}$

$= 2 \times 96500 \times 1.43$

= ●276 kJ

(ii) Suggest the material(s) to be used for the anode.

● Zinc

(iii) After prolonged usage, an alkaline battery will eventually 'run out' and can no longer be used. State and explain whether this could be due to hydroxide ions being depleted.

● It <u>cannot</u> be due to the depletion of hydroxide ions. The number of moles of hydroxide ions consumed is the same as the number of moles of hydroxide ions formed, <u>therefore [OH^-] remains constant</u>.

or the overall equation is $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$, which is independent of OH^-.

(iv) Alkaline batteries are prone to leaking the electrolyte. When this occurs, typically a white crystalline salt structure will form at the ends of the battery after reaction with air. State the likely identity of this salt and explain how it is formed.

● Potassium carbonate **or** K_2CO_3.

● Leaked electrolyte contains <u>KOH, which absorbs CO_2 from the air</u> to form potassium carbonate in solution. Natural evaporation of water from the electrolyte causes the crystals to form.

[6]

[Total: 20]